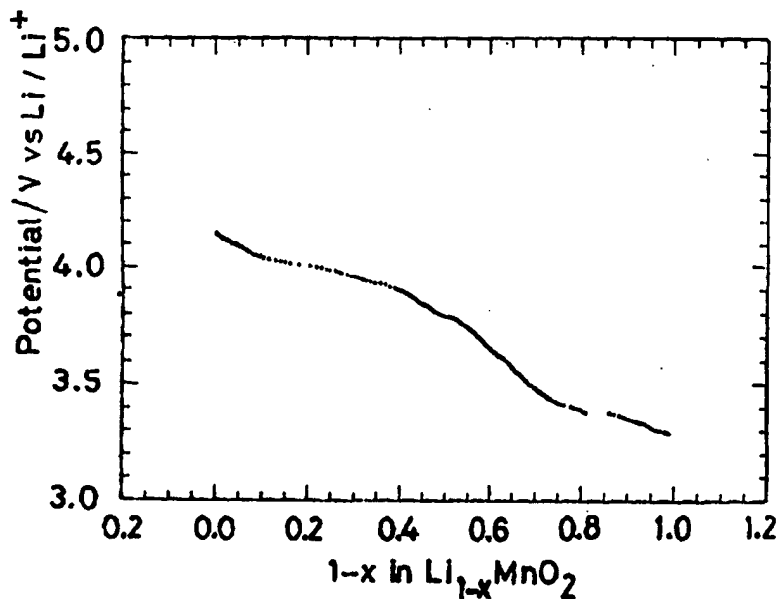




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01M 4/48, 4/50, C01G 45/02		A1	(11) International Publication Number: WO 97/26683
			(43) International Publication Date: 24 July 1997 (24.07.97)
(21) International Application Number: PCT/GB97/00031		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 8 January 1997 (08.01.97)			
(30) Priority Data: 9600772.9 15 January 1996 (15.01.96) GB			
(71) Applicant (for all designated States except US): THE UNIVERSITY COURT OF THE UNIVERSITY OF ST. ANDREWS [GB/GB]; St. Andrews, Fife KY16 9SS (GB).			
(72) Inventors; and		Published	
(75) Inventors/Applicants (for US only): BRUCE, Peter, George [GB/GB]; 14 Linden Avenue, Newport-on-Tay, Fife DD6 8DU (GB). ARMSTRONG, Anthony, Robert [GB/GB]; 5 James Street, St. Andrews, Fife KY16 9YA (GB).		With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(74) Agent: KEITH W. NASH & CO.; 90-92 Regent Street, Cambridge CB2 1DP (GB).			

(54) Title: IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL CELLS



(57) Abstract

A novel layered material for use in electrochemical cells is provided, together with a method for producing the layered material, and a cell having the layered material as the positive electrode. The material is of the form $\text{Q}_y\text{Mn}_y\text{M}_z\text{O}_2$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and the material has a layered structure. Methods of preparing the manganese oxide material are provided, using an ion exchange reaction or an ion removal reaction. Use of the material in an electrochemical cell is demonstrated.

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Title: Improvements in or Relating to Electrochemical Cells

Field of Invention

This invention concerns electrochemical cells and relates to a novel layered material for use in such cells, a method for producing the layered material, and a cell having the layered material as the positive electrode.

Background to the Invention

Electrochemical cells generally have a negative electrode, a positive electrode, and an electrolyte placed between the electrodes. The electrolyte is chosen so that transfer of ions between the two electrodes occurs, thus producing an electrical current. One example of an electrochemical cell is a rechargeable battery. The use of layered materials such as lithium cobalt oxide, LiCoO_2 , as the positive electrode in such a rechargeable battery is well established. The layered material LiCoO_2 consists of sheets of oxygen ions stacked one on top of the other. Between the first and second layers of oxygen are located the cobalt ions, with the lithium ions being located between the second and third oxygen layers. Use of LiCoO_2 in rechargeable batteries allows greater energy storage per unit weight and volume than is possible in conventional rechargeable batteries such as nickel-cadmium. However LiCoO_2 has disadvantages in that it is somewhat toxic, has limited energy storage capacity, and the cobalt containing materials from which it is produced are expensive and scarce.

Attempts have been made to use other compounds with a similar layered structure to that of LiCoO_2 , such as LiNiO_2 , and LiFeO_2 . EP 0 017 400 discloses a range of compounds having layers of the $\alpha\text{-NaCrO}_2$ structure. However, preparation of the materials according to the present invention is not taught and could not be achieved; see for example E. Rossen, C.D.W. Jones, and J.R. Dahn, "Structure and electrochemistry of $\text{Li}_x\text{Mn}_y\text{Ni}_{1-y}\text{O}_2$ ", Solid State Ionics, 57 (1992), 311-318.

It is one aim of the present invention to provide a novel layered manganese oxide material which can be used in electrochemical cells.

Summary of the Invention

According to one aspect of the present invention, there is provided a manganese oxide material, wherein the material is of the form $Q_qMn_yM_zO_2$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and the material has a layered structure.

A layered structure is one in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In general, each layer contains ions of one particular element, although the layer of Mn ions may contain M ions if present. Thus, when z is equal to zero and q is greater than zero, the layering will consist of sheets of oxide ions which are separated by alternating layers of Q ions and Mn ions, i.e. the layers order as a layer of oxide ions, a layer of Mn ions, a layer of oxide ions, a layer of Q ions and a layer of oxide ions; this is repeated throughout the structure.

Where z is not equal to zero, $y+z$ is preferably chosen to equal one. In such a material, the M ions will occupy sites in the Mn layers.

Q is preferably chosen from the Group I elements, i.e. K, Li, Rb.

Where z is not equal to zero, the element M is typically chosen from Group II elements, the transition elements or from Group III elements. Suitable elements include Be, Mg, Ca, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Al, Ga, P.

Accordingly in a particularly preferred material according to the invention, Q is an alkali metal ion, such as Rb, K or Li, and M is a transition metal ion.

Preferably Q is chosen to be Li, so that the material is of the form $Li_wMn_yM_zO_2$, where w is any number greater than zero.

The layered structure preferably possesses a crystal symmetry lower than rhombohedral. A preferred symmetry for the layered structure is monoclinic. The monoclinic structure possesses one 2-fold axis and/or one plane of symmetry, its unit cell possessing three unequal axes, one axis being perpendicular to the other two axes which are inclined at an oblique angle, β . In such a structure the Mn ions are not equally spaced from all nearest neighbour oxide ions, i.e. the three oxide ions in the adjacent upper layer and the three oxide ions in the adjacent lower layer, but rather are distorted from equal spacing so that the Mn-O bond distance varies. An equivalent view of this is that the layered structure comprises layers of MnO_6 polyhedra separated by layers of other ions, for example lithium ions.

Preferably the material is LiMnO_2 , having a layered monoclinic structure.

In a simple alternative the material may be of the form Mn_2O_3 , where the layers order as a layer of oxide ions, a layer of Mn ions; this being repeated throughout the structure. The layered structure of this material is rhombohedral, with the Mn ions being equally spaced from all nearest neighbour oxide ions, i.e. the three oxide ions in the adjacent upper layer and the three oxide ions in the adjacent lower layer, so that the Mn-O bond distance is constant. An equivalent view of this is that the layered structure comprises successive layers of MnO_6 octahedra.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing an intermediate material $\text{X}_x\text{Mn}_y\text{M}_z\text{O}_3$, where X is a group I element not being lithium, M is any element, x and y are each any number greater than zero, and z is any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form $\text{Li}_w\text{Mn}_y\text{M}_z\text{O}_3$, where w is any number greater than zero, and the material has a layered structure.

Preferably X is chosen to be Na, so that the intermediate material is of the form $\text{Na}_x\text{Mn}_y\text{M}_z\text{O}_3$.

More preferably y is equal to one and z is equal to zero, so that the intermediate material is of the form NaMnO_2 . The use of such an intermediate material results in production of a layered material of the form LiMnO_2 , having a layered monoclinic structure as described above.

The reactant may be any suitable lithium salt, such as LiBr or LiCl . Preferably the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux. Typically n -pentanol, n -hexanol or n -octanol are used as the reflux agent, with the reflux period being 6-8 hours.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing a precursor material $\text{Q}_q\text{Mn}_y\text{M}_z\text{O}_2$, where Q and M are each any element, q and y are each any number greater than zero, and z is any number greater than or equal to zero, by carrying out an ion removal reaction, so as to remove Q and produce a material of the form $\text{Mn}_y\text{M}_z\text{O}_2$, with a layered structure.

Ion removal is conveniently achieved by electrochemical extraction, using the precursor material as the working electrode in an electrochemical cell. This is of particular advantage in preparation of materials of the form Mn_yO_2 . For preparation of these materials, Q is preferably chosen from the Group I elements, such as Na , K , Rb . The Mn_yO_2 may be subsequently processed to insert lithium so as to produce $\text{Li}_x\text{Mn}_y\text{O}_2$.

According to another aspect of the invention, there is provided an electrochemical cell, wherein the positive electrode is of the form $\text{Li}_x\text{Mn}_y\text{M}_z\text{O}_2$, where M is any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero. The use of the manganese in the electrode avoids the need for use of cobalt or nickel which is of advantage as manganese is less toxic, more abundant and cheaper than cobalt and nickel.

Preferably y and q are equal to one, and z is equal to zero, with the preferred electrode material being LiMnO_2 .

A rechargeable battery is an example of an electrochemical cell with which the invention may be used.

The invention will now be described by way of example, and with reference to the accompanying Figures in which:

Figure 1 shows the observed diffraction data of the material obtained from the method according to the invention, and the fit of a theoretical diffraction pattern assuming a layered monoclinic model;

Figure 2 shows the observed diffraction data of the material obtained from the method according to the invention, and the fit of a theoretical diffraction pattern assuming a tetragonal spinel model;

Figure 3 shows a representation of LiMnO_2 assuming a monoclinic layered model;

Figure 4 shows a representation of LiMnO_2 assuming a tetragonal spinel model;

Figure 5 shows the voltage response of an electrolytic cell using $\text{Li}_{1-x}\text{MnO}_2$, as $1-x$ varies; and

Figure 6 shows the percentage of initial discharge capacity on successive discharge cycles of the cell.

Description

EXAMPLE 1

A material LiMnO_2 , being a preferred embodiment of the invention will now be described by way of example. The preparation of the material LiMnO_2 and the experimental verification of its structure and its properties as an electrode for an electrochemical cell will be described.

Preparation of LiMnO_2

Preparation of LiMnO_2 required two stages:

- 1) The preparation of the intermediate material, sodium manganese oxide, NaMnO_2 ; and
- 2) Ion exchange reaction.

Stage 1) is largely known from the literature, see Fuchs and Kemmler-Sack, Solid State

Ionics 68, 279, 1994. Stoichiometric quantities of sodium carbonate, Na_2CO_3 , and manganese (III) oxide, Mn_2O_3 , are weighed out, intimately mixed and ground under acetone in an agate mortar and pestle until a homogeneous mixture is obtained. The acetone is allowed to evaporate and the mixture transferred to a crucible and heated in a tube furnace at 700-730°C for 18-72 hours under flowing argon. The optimal heating time to ensure the best density and homogeneity of the resulting material is 48 hours.

After heating the sample is furnace cooled and then removed from the furnace. Phase purity of the resulting NaMnO_2 was confirmed by powder X-ray diffraction. Materials of the form $\text{NaMn}_x\text{M}_y\text{O}_2$ (where $\text{M} = \text{Be, Mg, Ca, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Al, Ga, P}$ etc) may be prepared by using the appropriate oxide to replace some of the Mn_2O_3 .

In stage 2), a 10 to 15 fold excess of lithium chloride, LiCl , i.e. 5g, or lithium bromide, LiBr , i.e 10g, is added to a round bottomed flask containing 100ml of either n-pentanol, n-hexanol, or n-octanol. 1g of the previously prepared NaMnO_2 is added to the mixture in the flask, a condenser attached and the mixture heated under reflux for a period of 6 to 8 hours. Refluxing temperatures are around 130°C for n-pentanol, 145-150°C for n-hexanol and 180-185°C for n-octanol. After cooling to room temperature, the product is filtered under suction, washed firstly with the appropriate alcohol and then with ethanol, and finally dried. Phase purity of the resulting product material was confirmed by powder X-ray diffraction.

The structure of the product produced according to the method was then determined by neutron diffraction. Determination of the structure by this method requires the observed diffraction data from a representative sample of the product to be compared to theoretical diffraction data for a variety of structural models. The correct structural model produces the best fit between theoretical and observed data. Typically trial models are selected by looking at the structures of similar families of compounds, or from the structures of the compounds that formed the product.

To analyse the structure of the material formed from the above described method, two models were tested. The first assumed that the layered monoclinic structure of the parent

NaMnO_2 was retained after the ion exchange reaction. The second model assumed a tetragonal spinel structure as adopted by $\text{Li}_2\text{Mn}_2\text{O}_4$, i.e. not a layered structure like the cobalt or nickel compounds discussed above but rather a completely different three dimensional structure. It should be understood that other compounds with the LiMnO_2 composition have been prepared in the past but with completely different structures. It is known that orthorhombic LiMnO_2 , low temperature "orthorhombic" LiMnO_2 and tetragonal spinel $\text{Li}_2\text{Mn}_2\text{O}_4$ may be produced.

Time-of-flight powder neutron diffraction data were collected on the POLARIS high intensity, medium resolution diffractometer at the ISIS pulsed source at the Rutherford Appleton Laboratory. Data from the highest resolution backscattering bank of detectors were used for structural analysis.

The observed diffraction data were compared with theoretical data for each of the two models. The fit of the real and theoretical data for the monoclinic layered structure is shown in Figure 1. Figure 3 shows a representation of this model as it is thought to relate to LiMnO_2 ; MnO_6 polyhedra shown, with Li ions as circles. The structure shown in Figure 3 is layered and related to the structure of LiCoO_2 , described above. However due to the presence of the Jahn-Teller active ion Mn^{3+} , the structure is distorted from that of LiCoO_2 . The main difference is that the crystal symmetry is lowered from rhombohedral (LiCoO_2) to monoclinic (LiMnO_2). The MnO_6 polyhedra have a lower symmetry than that of the CoO_6 polyhedra as the MnO_6 polyhedra are considerably distorted compared with those of CoO_6 . The CoO_6 polyhedra are octahedral. Table 1 below shows relative site occupancies and positions of the atoms within this material when using the monoclinic structure.

The fit of the real and theoretical data in the case of the tetragonal ($\text{Li}_2\text{Mn}_2\text{O}_4$ spinel) structure is shown in Figure 2. Figure 4 shows a representation of the model applied to LiMnO_2 ; MnO_6 polyhedra are shown, with Li ions as light circles and Mn ions as dark circles. Table 2 below shows the relative site occupancies and positions of the atoms if this model applied.

Wyckoff						
Atom	symbol	x	y	z	B _{eq}	Site Occupancy
Li1/Mn1	2d	0	0.5	0.5	2.4(2)	0.91/0.09(4)
Li2/Mn2	2a	0	0	0.0	0.72(6)	0.10/0.90(3)
O1	4i	0.2723(3)	0	0.7706(2)	0.68(4)	1

$a=5.4387(7)$, $b=2.80857(4)$, $c=5.3878(6)\text{\AA}$, $\beta=116.006(3)^\circ$

$\chi^2=11.83$ ($R_{\text{exp}}=0.60\%$, $R_p=1.86\%$, $R_w=2.06\%$, $R_1=3.98\%$)

Table 1: Results obtained on fitting a layered monoclinic structure to the observed data, space group $C2/m$ (no. 12).

Wyckoff						
Atom	symbol	x	y	z	B _{eq}	Site Occupancy
Li	8c	0	0	0	3.6(5)	1
Mn	8d	0	0	0.5	0.12(5)	1
O	16h	0.0	0.4826(5)	0.2552(3)	0.39(5)	1

$a=5.66632(6)$, $b=5.66632$, $c=9.1852(2)\text{\AA}$

$\chi^2=63.50$ ($R_{\text{exp}}=0.60\%$, $R_p=4.00\%$, $R_w=4.79\%$, $R_1=6.58\%$)

Table 2: Results obtained on fitting a tetragonal structure to the observed data, space group $I4_1/amd$ (no. 141).

It can be seen from the analysis presented in Tables 1 and 2, and Figures 1 and 2, that the best fit, i.e. that with least error, see χ^2 value and R values, is obtained for the monoclinic structure. The method according to the invention has thus produced monoclinic layered LiMnO_2 .

The performance of the monoclinic LiMnO_2 in an electrochemical cell was then investigated. Investigation into the properties of LiMnO_2 was undertaken using a three electrode cell composed of lithium metal counter and reference electrodes. The working electrode, i.e. the positive electrode was fabricated by compressing powdered LiMnO_2 .

(80%), carbon black (13.3%) and PTFE (6.7%) on to a metal grid. The electrolyte was LiClO_4 dissolved in propylene carbonate. LiClO_4 was rigorously dried by heating under vacuum at 150°C and the solvent was distilled using a Fischer HMS 500C distillation apparatus with 90 theoretical plates. The cell with an electrolyte solution of 1M LiClO_4 in propylene carbonate was subjected to charging at a current of $10\mu\text{Acm}^{-2}$.

The resulting voltage of this cell as a function of lithium content is shown in Figure 5. Two voltage plateaux are visible; one at 3.4V, the other at 4V vs. $\text{Li}^+(1\text{M})/\text{Li}$. The maximum voltage of 4.1V is obtained for $1-x=0$, i.e. for MnO_2 . The cell was cycled at a constant current of 0.5mAcm^{-2} between the potential limit 3.4 and 4.3 V to simulate the behaviour of a rechargeable battery. This cycling data is shown in Figure 6, with the percentage of initial discharge capacity shown for successive cycles. It will be seen that capacity declines on cycling. However the voltage range has not been optimised and includes both plateaux. Figure 6 demonstrates that lithium can be chemically or electrochemically extracted from LiMnO_2 and reinserted into this compound, i.e. it is an intercalation/insertion electrode.

As demonstrated in the above preparation of LiMnO_2 , it is possible to ion exchange sodium for lithium in NaMnO_2 . As a variant of this, sodium can be electrochemically or chemically extracted from this NaMnO_2 yielding a material with a layered structure and the formula MnO_2 . Typically this involves an electrochemical cell in which NaMnO_2 is the working electrode and passing a constant current through the cell. Such a cell may be a cell such as that described above for LiMnO_2 , but using sodium counter and reference electrodes and a solution of NaClO_4 in propylene carbonate. The electrode material is thus oxidised, removing sodium and converting Mn^{3+} to Mn^{4+} , producing MnO_2 . An alternative synthesis of LiMnO_2 may then be carried out by insertion of lithium into the MnO_2 .

EXAMPLE 2

SYNTHESIS OF $\text{NaMn}_{1-x}\text{M}_x\text{O}_2$

Two methods were used to prepare compounds of the form $\text{NaMn}_{1-x}\text{M}_x\text{O}_2$. The first

preparation involved weighing stoichiometric quantities of sodium carbonate (Na_2CO_3) (or a slight Na_2CO_3 excess) and manganese (III) oxide (Mn_2O_3) and the appropriate other metal oxide e.g. cobalt oxide (Co_3O_4), nickel (II) oxide (NiO), iron (III) oxide (Fe_2O_3) and intimately mixing and grinding under acetone in an agate mortar and pestle until a homogeneous mixture was obtained. Once the acetone had evaporated the mixture was transferred to a crucible and heated in a furnace at 650-750°C for 10-72 hours in air. The sample was cooled to below 200°C before removal from the furnace. Phase purity was confirmed by powder X-ray diffraction.

The second preparation involved weighing out appropriate quantities of manganese (II) acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and the other metal salt e.g. cobalt (II) acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) or nickel (II) acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and dissolving them in distilled water. A stoichiometric quantity of sodium carbonate (Na_2CO_3), or a slight Na_2CO_3 excess, was weighed out into a separate vessel and dissolved in distilled water. The two solutions were then mixed and stirred. The water was then removed on a rotary evaporator. The resulting solid was transferred to a crucible and heated in a furnace at 180-300°C for 2-24 hours in air. The sample was cooled to below 100°C before removal from the furnace; it was then ground in an agate mortar and pestle, transferred to a crucible with a lid and heated in a furnace at 500 - 850°C for 1-60 hours in air. Samples were removed from the furnace at this temperature or after cooling. Phase purity was confirmed by powder X-ray diffraction.

Subsequent processing of either preparation was as described in Example 1 above.

Claims

1. A manganese oxide material, wherein the material is of the form $Q_yMn_zM_xO_2$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and the material has a layered structure.
2. A manganese oxide material according to claim 1, wherein $y+z$ is chosen to equal one.
3. A manganese oxide material according to claim 1 or claim 2, wherein Q is chosen from Group I elements.
4. A manganese oxide material according to any of the preceding claims, wherein Q is an alkali metal ion and M is a transition metal ion.
5. A manganese oxide material according to any of the preceding claims, wherein Q is chosen to be Li, so that the material is of the form $Li_wMn_zM_xO_2$, where w is any number greater than zero.
6. A manganese oxide material according to any of the preceding claims, wherein the layered structure possesses a crystal symmetry lower than rhombohedral.
7. A manganese oxide material according to any of the preceding claims, wherein the material has a layered monoclinic structure.
8. A manganese oxide material according to any of the preceding claims, wherein the material is $LiMnO_2$, having a layered monoclinic structure.
9. A manganese oxide material according to claim 1, wherein the material is of the form Mn_xO_2 .
10. A method of preparing a manganese oxide material, comprising processing an

intermediate material $X_xMn_yM_zO_2$, where X is a group I element not being lithium, M is any element, x and y are each any number greater than zero, and z is any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form $Li_xMn_yM_zO_2$, where w is any number greater than zero, and the material has a layered structure.

11. A method according to claim 10, wherein X is chosen to be Na, so that the intermediate material is of the form $Na_xMn_yM_zO_2$.

12. A method according to claim 10 or claim 11, wherein y is equal to one and z is equal to zero, so that the intermediate material is of the form $NaMnO_2$.

13. A method according to any of claims 10 to 12, wherein the reactant is a lithium salt.

14. A method according to any of claims 10 to 13, wherein the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux.

15. A method of preparing a manganese oxide material, comprising processing a precursor material $Q_xMn_yM_zO_2$, where Q and M are each any element, x and y are each any number greater than zero, and z is any number greater than or equal to zero, by carrying out an ion removal reaction, so as to remove X and produce a material of the form $Mn_yM_zO_2$, with a layered structure.

16. A method according to claim 15, wherein the ion removal reaction is achieved by using the precursor material as the working electrode in an electrochemical cell.

17. A method according to claim 15 or claim 16, wherein the material is of the form Mn_yO_2 .

18. An electrochemical cell, wherein the positive electrode is of the form $Li_xMn_yM_zO_2$, where M is any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero.

19. An electrochemical cell according to claim 18, wherein y and q are equal to one, and z is equal to zero, with the electrode material being LiMnO_2 .
20. A rechargeable battery, comprising an electrochemical cell according to claim 18 or claim 19.
21. A method of preparing a manganese oxide material and a manganese oxide material for electrochemical cells substantially as herein described.
22. An electrochemical cell having an electrode of manganese oxide material substantially as herein described.

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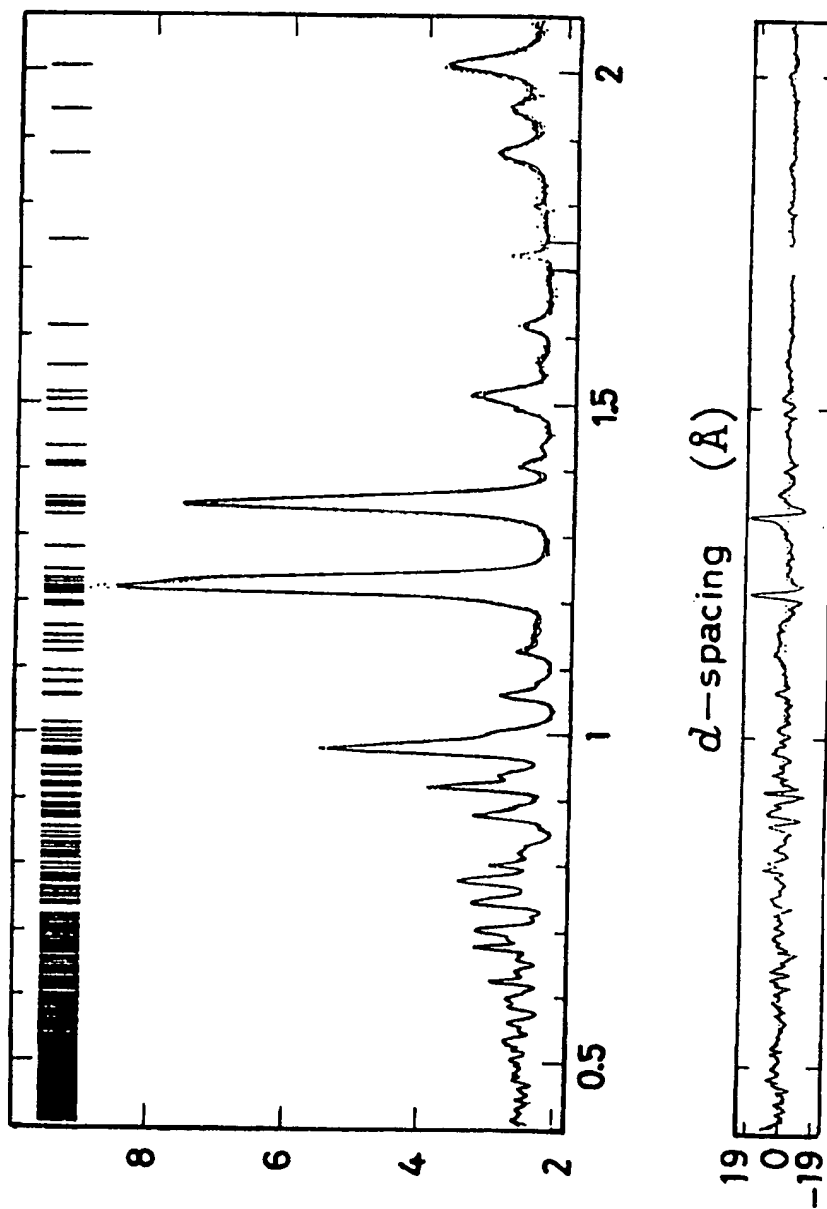


Fig. 1

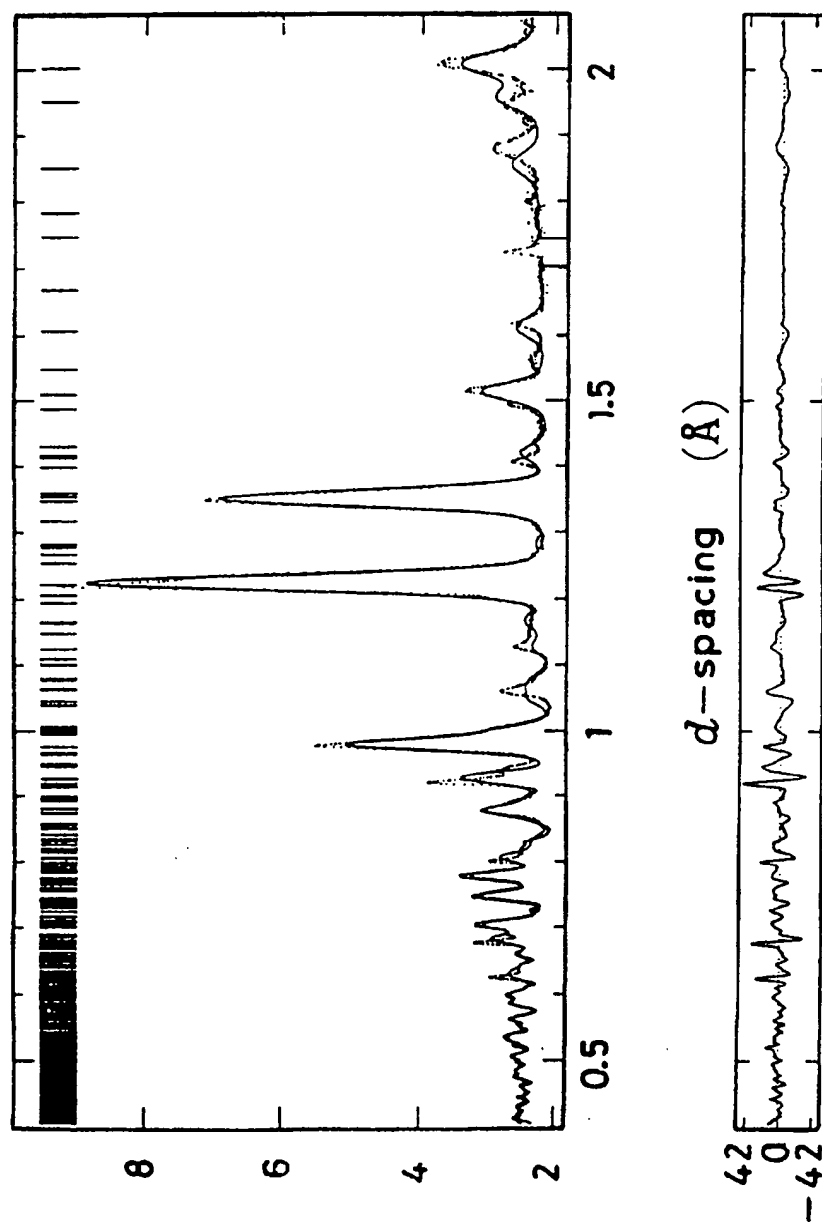


Fig. 2

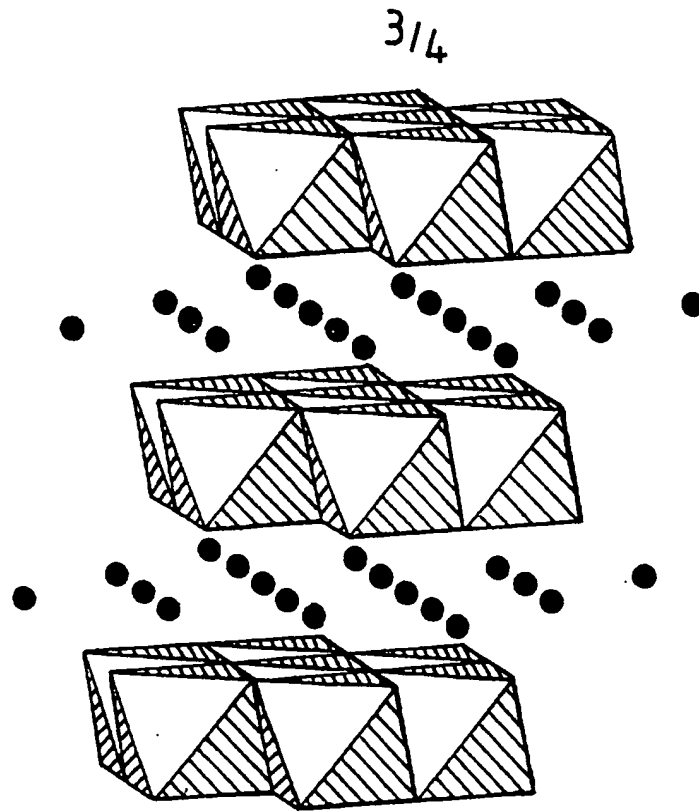


Fig. 3

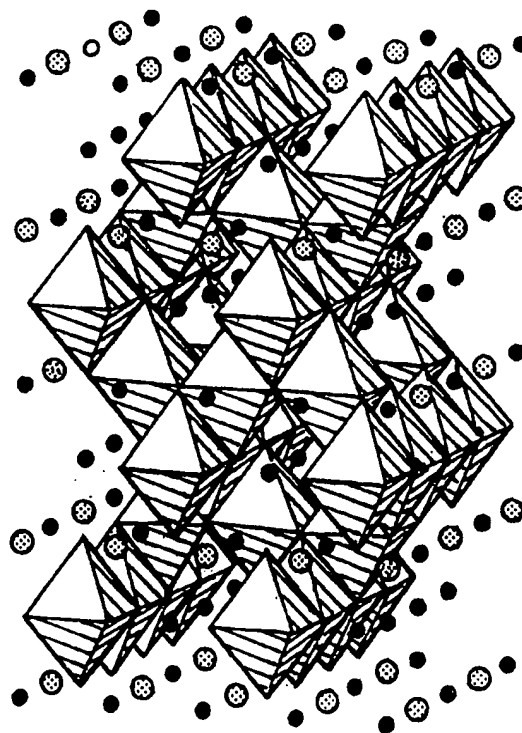


Fig. 4

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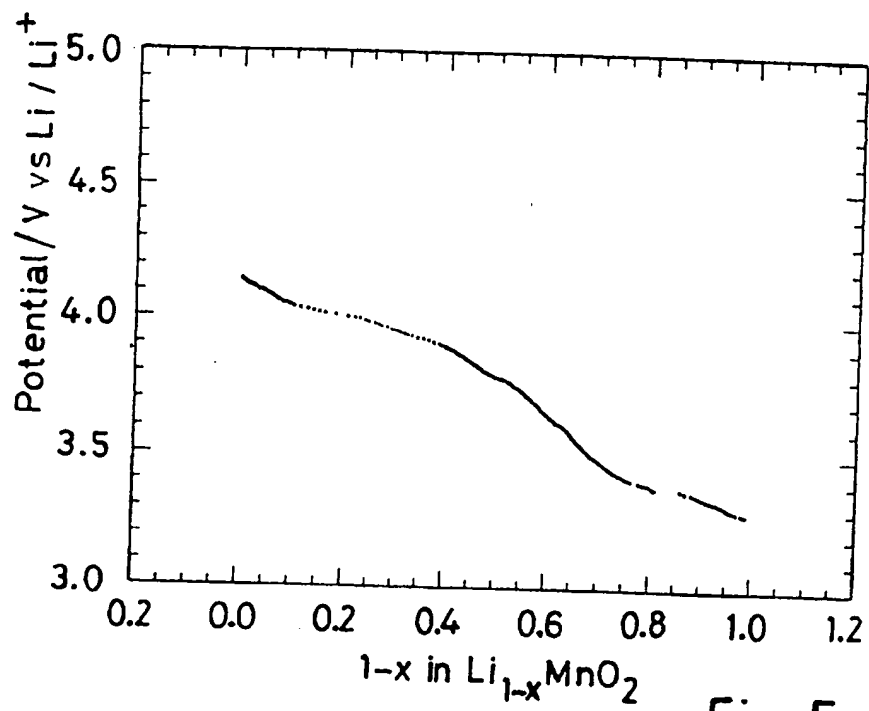


Fig. 5

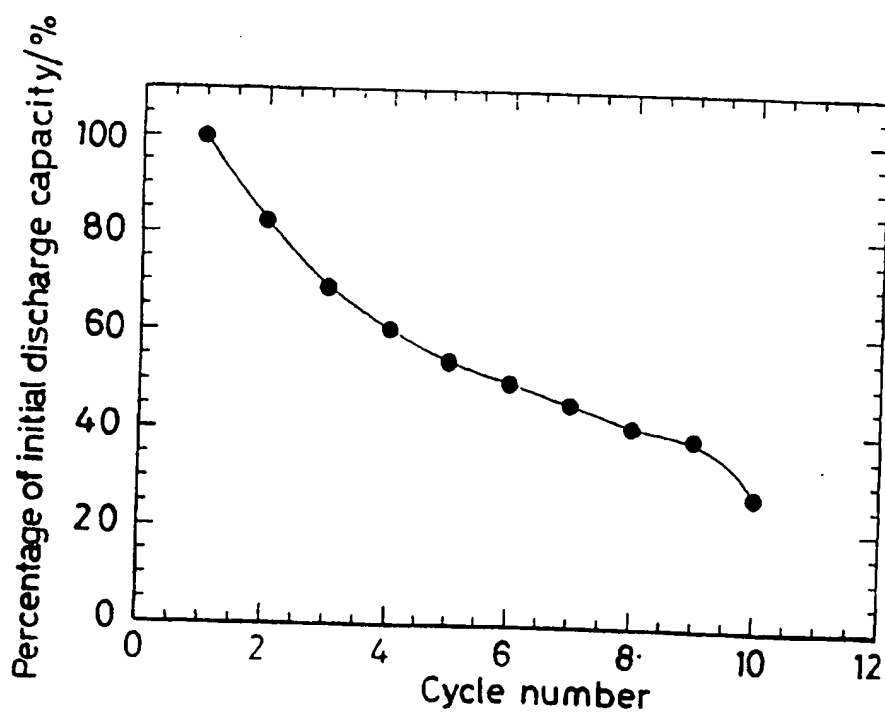


Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/00031

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/48 H01M4/50 C01G45/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 242 898 A (TECHNOLOGY FINANCE CORP) 16 October 1991 see claims 1-22 ---	1-5, 18, 20
X	EP 0 581 290 A (TOSOH CORP) 2 February 1994 see examples 7, 8 ---	1, 15-17
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 252 (E-1547), 13 May 1994 & JP 06 036799 A (SANYO ELECTRIC CO LTD), 10 February 1994, see abstract ---	18, 19
A	EP 0 624 552 A (MOLI ENERGY 1990 LTD) 17 November 1994 see claims 1-12; examples 1-4 ---	10-14, 18-20
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

22 April 1997

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European Patent Office, P.O. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/00031

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 656 667 A (MOLI ENERGY 1990 LTD) 7 June 1995 see claims 1-16 ---	1-22
A	EP 0 556 555 A (MATSUSHITA ELECTRIC IND CO LTD) 25 August 1993 see claims 1-10; examples 1-8 ---	1-22
P,X	US 5 558 961 A (DOEFF MARCA M ET AL) 24 September 1996 see column 6, line 49 - column 7, line 17; claims 1-31 -----	10,11,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/00031

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2242898 A	16-10-91	DE 4111459 A	17-10-91
		FR 2660918 A	18-10-91
		JP 6072708 A	15-03-94
		US 5160712 A	03-11-92

EP 0581290 A	02-02-94	JP 6227820 A	16-08-94

EP 0624552 A	17-11-94	CA 2096264 A	15-11-94
		JP 6349494 A	22-12-94

EP 0656667 A	07-06-95	CA 2102738 A	10-05-95
		JP 7192768 A	28-07-95
		US 5518842 A	21-05-96

EP 0556555 A	25-08-93	JP 5299092 A	12-11-93
		US 5370948 A	06-12-94

US 5558961 A	24-09-96	NONE	

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